(DE 3816807 - DE 3824879) (4+5a)

OD- 334470 /89

89-334470/46 C02 SCHD 13.05.88
SCHERING AG *EP -342-150-A
19.07.88-DE-824879 (+DE-816807) (15.11.89) A01n-43/82
C07d-261/10 C07d-263/46 C07d-271/10 C07d-285/12
New azole ether(s) - useful as pesticides esp. against nematodes
C89-148240 R(AT BE CH DE ES FR GB GR IT LI LU NL SE)

Other Priorities: 13.06.88-DE-820456 15.06.88-DE-820628

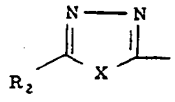
C(7-H1, 7-H2, 12-N1) 3 C0066

Azole ethers of formula (I) are new:

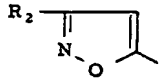
A — SR_1

(I)

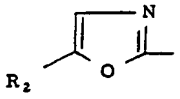
A = a gp. of formula (a) - (c):



(a)

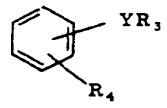


(b)



(c)

when A = gp. (a):
X = O or S; and either
(i) R_1 = CF_2Br, $-CH_2-CF_3$, $-CF_2-CF_2Br$, $-CH_2CF_2CF_2H$ or CH_2CH_2F; and
R_2 = Ph, biphenyl or naphthyl, each opt. substd. by halogen, 1-4C alkyl, 1-4C alkoxy, 1-4C alkylthio, 1-4C haloalkyl, 1-4C haloalkoxy, 1-4C haloalkylthio, NO_2 or CN; or
(ii) R_1 = 1-12C alkyl or 2-12C alkenyl each opt. substd. by one or more halogen; and
R_2 = gp. of formula (d):



(d)

Y = O or S;
R_3 = 1-12C fluoroalkyl or 2-12C fluoroalkenyl;
R_4 = H, halogen, 1-6C alkyl, 1-6C alkoxy, 1-6C alkylthio,

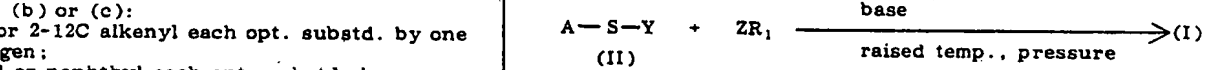
EP-342150-A+

1-4C haloalkyl, 1-4C haloalkoxy, 1-4C haloalkylthio, NO_2 or CN;
when A = gp. (b) or (c):
R_1 = 1-12C alkyl or 2-12C alkenyl each opt. substd. by one or more halogen;
R_2 = Ph, biphenyl or naphthyl each opt. substd. by one or more halogen, 1-4C alkyl, 1-4C alkoxy, 1-4C alkylthio, 1-4C haloalkyl, 1-4C haloalkoxy, 1-4C haloalkylthio, NO_2 or CN.

MORE SPECIFICALLY
A = gp. (a); and
(i) R_1 = bromodifluoromethyl;
R_2 = phenyl opt. substd. (pref. of the 4-position) by halo, 1-4C alkoxy or 1-4C alkyl; or
(ii) R_1 = 1-4C fluoroalkyl or 2-4C fluoroalkenyl opt. substd. by bromo;
R_2 = phenyl substd. (pref. in the 4-position) by 1-4C fluoroalkoxy.

USE/ADVANTAGE
(I) are useful as pesticides, esp. against nematodes. They also show good activity against biting and sucking insects and their eggs and mites. The cpds. have good plant compatibility.
Appln. rate is 0.03 - 10 kg (pref. 0.3 - 6 kg) per ha.

PREPARATION



(II) base, raised temp., pressure → (I)

Z = leaving gp.;
Y = H, NH_4 or alkali metal.

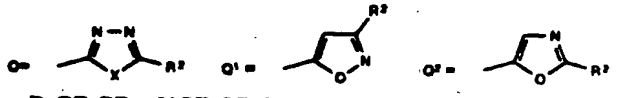
EXAMPLE
80% suspension of NaH (1.65 g), washed with toluene, was suspended in DMF (20 ml). At 5-10°C a soln. of 5-(4-chlorophenyl)-1,3,4-thiadiazole-2-thiol (5.5 g) in DMF (40 ml) was added and stirred for 30 min. at 10°C. Dibromodifluoromethane (11.6 g) was added dropwise and the mixt. stirred for 3 hr. at 10°C. After work up and purification by flash column chromatography, 2-bromodifluoromethylthio-5-(4-chlorophenyl)-1,3,4-thiadiazole (2.4 g, 13.2%), m. pt. 72°C, was obtd. (14pp1917EDDwgNo0/0).
(E) ISR: EP-217747 EP-220025 US4001228.

3-02 4 5-01

(I) 8JG, 8ΦG, 8MG, 9GD, 10G 9GG, 18Z

EP-342150-A

112: **198390z Substituted azole thioethers, their preparation and use as pesticides.** Huebl, Dieter; Buehmann, Ulrich; Pieroh, Ernst; Joppien, Hartmut (Schering A.-G.) **Eur. Pat. Appl. EP 342,150** (Cl. C07D285/12), 15 Nov 1989, DE Appl. 3,816,807, 13 May 1988; 14 pp. ASR¹ (I; A = azolyl groups Q - Q²; R¹ = $BrCF_2$,



CF_3CH_2, $BrCF_2CF_2$, $HCF_2CF_2CH_2$, FCH_2CH_2, (un)substituted C_{1-12} alkyl, (un)substituted C_{2-12} alkenyl; R² = (un)substituted Ph, biphenylyl, naphthyl, substituted phenyloxy, -phenylthio; X = O, S) were prepd. At 5-10° 5-(4-chlorophenyl)-1,3,4-thiazole-2-thiol in DMF was added NaH in paraffin and the mixt. stirred for 30 min at 10°. CBr_2F_2 was added dropwise and the mixt. stirred for 3 h at 10° to give I (A = Q; X = S; R¹ = BrF_2C; R² = 4-ClC_6H_4) (II). Nematode attack by *Meloidogyne incognita* was 100% controlled by II at 25 mg/L soil.

11-01 : 126 767-00-8
12-01 : -36-0
13-01 : -46-2

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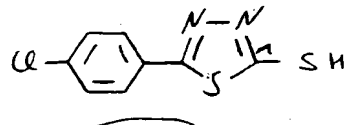
VERSCHLUSSELT	KORRIGIERT	BEMERKUNGEN	BLATT-NR.	BLATTZAHL
Kozmierczak Bolg	NEK	CA.....:	1	2

F

Preparation / Example



3-02

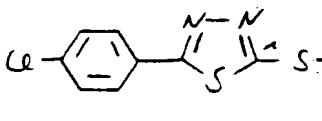
Natt

$Br-CF_2Br$ (4)

$Br-CH_2-CF_3$ (7)

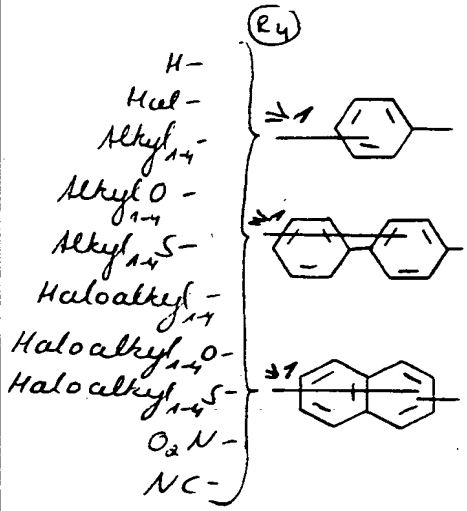
$Br-CF_2-CF_2Br$ 8

$Br-CF(CF_3)_2$ 9



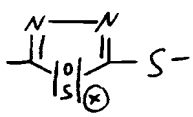
- $-CF_2Br$ 5-01
- $-CH_2-CF_3$
- $-CF_2-CF_2Br$
- $-CF(CF_3)_2$

10-01



- H-
- Hal-
- $Alkyl_{1-4}$-
- $Alkyl_{1-4}O$-
- $Alkyl_{1-4}S$-
- $Haloalkyl_{1-4}$-
- $Haloalkyl_{1-4}O$-
- $Haloalkyl_{1-4}S$-
- O_2N-
- NC-

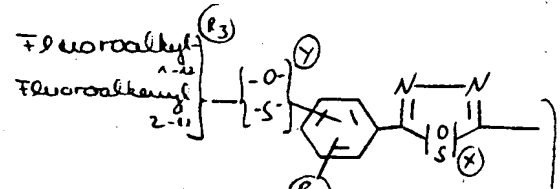
R_4, R_2



S-

R_1:
- CF_2Br
- CH_2CF_3
- CF_2CF_2Br
- $CH_2CF_2CF_2H$
- CH_2CH_2F

1-01



Fluoroalkyl$_{2-12}$

Fluoroalkenyl$_{2-12}$

R_3, Y: -O-, -S-

R_4

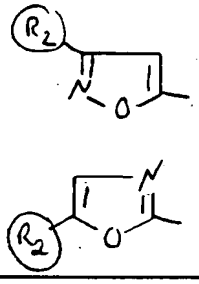
Fluoroalkyl$_{1-4}O$-

F_3CO-

F_2HCO-

F_3CCH_2O-

$F_2HCCF_2CH_2O$-



S

R_1:
- $Alkyl_{1-12}$
- $Alkenyl_{2-12}$
- $Haloalkyl_{1-12}$
- $Fluoroalkyl_{1-4}$ — H, Br
- $Haloalkenyl_{2-12}$
- $Fluoroalkenyl_{2-4}$ — H, Br
- CHF_2, CF_3
- CF_2Br
- CF_2CF_2Br
- $CF(CF_3)_2$
- $CH_2CH_2-CF=CF_2$
- $CF=CF-CF_3$

6-01